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Aqueous polymer dispersions*Abstract of the disclosure:*

Aqueous polymer dispersions, obtainable by polymerizing, in aqueous medium by the free radical emulsion polymerization method, a mixture of monomers which contains from 10 to 100 % w/w of halogen-containing monomers, adjusting the pH of the aqueous phase of the resulting aqueous polymer dispersion to a value of from 5 to 10 by the addition of ammonia and primary and secondary amines of different basic agents and adding, based on the mixture of monomers, from 0.005 to 1 % w/w of at least one active ingredient selected from the group consisting of benzaldehyde, derivatives of benzaldehyde having one or two C₁-C₄ alkyl radicals on the aromatic nucleus, benzyl alcohol, camphor, esters derived from formic acid and C₃-C₆ alkanols, C₁₀-C₂₂-unsaturated fatty acids, tetraalkyl orthosilicates containing alkyl radicals of from 1 to 4 carbon atoms, bis(4-hydroxyphenyl)-sulfone, citric acid and the salts thereof as well as salts of guanidine with organic or inorganic acids, both the addition of the basic agents and that of at least one active ingredient being possible prior to, during, and/or subsequently to the emulsion polymerization.

yellowing aqueous polymer dispersions obtainable by polymerizing, in aqueous medium by the free radical emulsion polymerization method, a mixture of monomers which contains from 10 to 100 % w/w of halogen-containing monomers, in the presence of from 0.5 to 6 % w/w, based on the mixture of monomers, of exclusively anionic and/or non-ionic interfacially active substances, and adjusting the pH of the aqueous phase of the resulting aqueous polymer dispersion to a value of from 5 to 10 by the addition of ammonia and primary and secondary amines of different basic agents. A disadvantage of these dispersions and films produced therefrom is that their discoloration characteristics with reference to time are not entirely satisfactory.

The prior German Patent Application P 40 24 150.5 relates to non-yellowing aqueous polymer dispersions obtainable by polymerizing, in aqueous medium by the free radical emulsion polymerization method, a mixture of monomers which contains from 10 to 100 % w/w of halogen-containing monomers, adjusting the pH of the aqueous phase of the resulting aqueous polymer dispersion to a value of from 5 to 10 by the addition of ammonia and primary and secondary amines of different basic agents and adding, based on the mixture of monomers, from 0.005 to 1 % w/w of at least one active ingredient selected from the group consisting of glycerol, pivalic acid, paraldehyde, 2,6-di-tert-butyl-p-cresol, benzophenone, alkyl-substituted benzophenones, thiosulfuric acid and salts thereof as well as oxalic acid and salts thereof, thiosulfuric acid and salts thereof being highly recommended for use as active ingredients.

It is thus an object of the present invention to provide an aqueous polymer dispersion containing polymerized units of halogen-containing monomers in the polymeric phase, whose pH is adjusted to a value of from 5 to 10 by the addition of basic agents and which, as also film formed therefrom, shows a very satisfactory low level of discoloration even after prolonged storage, as a result of the addition of an active ingredient other than epoxides and other than the active ingredients cited in the prior German application P 40 24 150.5

Accordingly, we have found the aqueous polymer dispersion defined above. The efficacy of the aforementioned active substances is at least equivalent to that of thiosulfuric acid and salts thereof. It is particularly advantageous to use, as active ingredient, benzaldehyde, camphor, benzyl alcohol, the ester derived from formic acid and n-butanol, oleic acid, tetraethyl orthosilicate and bis(4-hydroxyphenyl)-sulfone, and especially citric acid and salts thereof, eg the alkali metal salts, as well as the salts of guanidine with inorganic mineral acids. Especially the last two classes of compounds are more effective than thiosulfuric acid and its derivatives, whilst within these classes pure citric acid and the salts of guanidine with

hydrochloric acid, sulfuric acid, phosphoric acid, carbonic acid and water are of particular significance, particularly the salt of guanidine with hydrochloric acid.

Preferred halogen-containing monomers are vinyl bromide, vinyl chloride and vinylidene chloride, of which vinyl chloride and vinylidene chloride are particularly preferred. Suitable comonomers are, for example, esters of acrylic or methacrylic acid with aliphatic alcohols containing from 1 to 10 carbon atoms, the methyl, ethyl, isopropyl, n-butyl, isobutyl-, tert-butyl, n-hexyl, and 2-ethylhexyl esters being preferred. Other suitable comonomers are α,β -monoethylenically unsaturated carboxylic acids such as acrylic and methacrylic acids, vinyl esters of lower alkanecarboxylic acids such as vinyl acetate and vinyl propionate, nitriles of lower α,β -monoethylenically unsaturated carboxylic acids such as acrylonitrile and methacrylonitrile as well as the amides of these carboxylic acids, acrylates and methacrylates with lower polyhydric alcohols, and unsaturated sulfonic and phosphonic acids, further examples being lower mono-unsaturated or polyunsaturated hydrocarbons such as ethylene, propene and butadiene. Preferably, the monomer mixture to be polymerized contains, based on the total amount of monomers, from 20 to 90 % w/w of halogen-containing monomers.

Suitable polymerization initiators are primarily inorganic peroxides such as sodium, potassium, and ammonium peroxydisulfates, and hydrogen peroxide. Other suitable compounds comprise azo compounds such as 2,2'-azobisisobutyronitrile as well as organic peroxides such as dibenzoyl peroxide, tert-butyl perpivalate or hydroperoxides such as tert-butyl hydroperoxide and, if desired, combined systems composed of at least one organic reducing agent and at least one peroxide and/or hydroperoxide, eg tert-butyl hydroperoxide and the Na salt of hydroxymethanesulfonic acid, as well as combined systems which additionally contain a small amount of a metal compound which is soluble in the polymerisation medium and whose metallic component can occur in more than one valence stage, eg ascorbic acid/iron(II) sulfate/sodium peroxydisulfate, whilst instead of ascorbic acid the Na salt of hydroxymethanesulfonic acid, sodium sulfite, sodium bisulfite or sodium metabisulfite are also frequently used.

The amount of polymerization initiators used in the emulsion polymerization is preferably kept at a low level and is usually from 0.05 to 1 % w/w, based on the monomers. The content thereof is preferably from 0.1 to 0.3 % w/w. Amounts of up to 10 % w/w are less preferred.

Emulsifiers used may be anionic, cationic, and non-ionic emulsifiers as well as compatible mixtures thereof. The content thereof, by weight, is usually from 0.05 to 10 % w/w based on the total weight of the monomers to be polymerized. It is

particularly advantageous to use exclusively non-ionic and anionic emulsifiers and mixtures thereof.

Preferably used non-ionic emulsifiers are ethoxylated alkanols (degree of ethoxylation: from 2 to 100, alkyl radical: C_8-C_{36}), ethoxylated alcohols containing from 1 to 4 olefinic double bonds (degree of ethoxylation: from 2 to 100, chain length: C_8-C_{36}), ethoxylated mono-, di- oder tri-alkylphenols and mono-, di- oder tri-alkylnaphthols (degree of ethoxylation: from 2 to 100, alkyl radical: C_4-C_{36}), ethoxylated aliphatic monocarboxylic acids (degree of ethoxylation: from 6 to 50, alkyl radical: C_8-C_{24}) and ethoxylated monocarboxylic acids containing from 1 to 4 olefinic double bonds (degree of ethoxylation: from 6 to 50, alkyl radical: C_8-C_{24}).

Anionic emulsifiers which may be used to advantage are the alkali metal and ammonium salts of the sulfated derivatives of alkanols containing from 6 to 18 carbon atoms, alcohols containing from 6 to 18 carbon atoms and from 1 to 4 olefinic double bonds, ethoxylated alkanols (degree of ethoxylation: from 4 to 30, alkyl radical: $C_{12}-C_{18}$), ethoxylated alcohols containing from 1 to 4 olefinic double bonds (degree of ethoxylation: from 4 to 30, alkyl radical: $C_{12}-C_{18}$) and of ethoxylated alkyl phenols (degree of ethoxylation: from 4 to 30, alkyl radical: C_8-C_{14}), the alkali metal and ammonium salts of saturated and unsaturated carboxylic acids (chain length: C_8-C_{24}), the alkali metal and ammonium salts of alkylsulfonic acids containing from 12 to 18 carbon atoms as well as the corresponding salts of alkylarylsulfonic acids (alkyl radical: $C_{10}-C_{18}$) and of esters of sulfosuccinic acid with alcohols containing from 4 to 18 carbon atoms.

Protective colloids may also be used along with emulsifiers as interfacially active substances for the emulsion polymerization. Examples of suitable protective colloids are high molecular weight compounds such as poly(vinyl alcohol)s, poly(vinyl pyrrolidone)s, cellulose derivatives, polyacrylamides, polymethacrylamides, poly(carboxylic acid)s or the alkali metal or ammonium salts thereof. Furthermore, chain-stoppage modifiers may be used in the emulsion polymerization process.

It is preferred to use initiators and surface-active substances such as do not contain any ammonium ions.

The emulsion polymerization temperature is usually from 30° to 90 °C. However, dispersions of the invention which are particularly free from discoloration are obtained when the emulsion polymerization temperature is from 50° to 70 °C. The polymerization medium may consist either of water only or of a mixture of water and one or more liquids miscible therewith, such as methanol. We prefer to use

water only. The emulsion polymerization can be carried out as a batch process or in the form of a continuous-feed process using both cascade and gradient methods. We prefer to use a continuous-feed process, in which there is initially placed in the reaction vessel a portion of the polymerization ingredients, which are heated to the polymerization temperature, after which the remainder is fed in continuously, in stages, or by a method employing an overall concentration gradient, via separate feeds, one or more of which contains the monomers as pure substance or in the form of an emulsion. The solids content of the resulting aqueous polymer dispersion is generally from 5 to 60 % w/w.

Primarily suitable basic agents for raising the pH are metal salts of weak acids, eg acetates, formates, or carbonates of alkali metals, tertiary amines such as triethylamine, and especially hydroxides and oxides of alkali metals and alkaline-earth metals such as KOH, NaOH and $\text{Ca}(\text{OH})_2$, of which $\text{Ca}(\text{OH})_2$ is particularly preferred

Surprisingly, both the aqueous polymer dispersions of the invention and films produced therefrom show even after prolonged storage substantially no discoloration.

Examples

a) Manufacture of starting dispersions D 1 to D 8

D 1: a mixture of 25 kg of water, 0.02 kg of emulsifier I, 0.03 kg of sodium peroxydisulfate $8\text{Na}_2\text{S}_2\text{O}_8$ and 0.0005 kg of iron(II)sulfate heptahydrate $8\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was heated to the polymerization temperature, ie 50 °C and intermixed with 5 % of a feed 1 as well as 5 % of a feed 2 and kept at 50 °C for 15 minutes. The remaining amount of feed 1 as well as the remaining amount of feed 2 and a feed 3 were then added continuously and concurrently over a period of 3.5 hours while keeping the mixture at the polymerization temperature. A feed 4 was then added continuously over a period of 30 minutes at 50 °C and likewise a feed 5 over a period of 1 hour. Polymerization was then continued at room temperature with the addition of a mixture of 0.12 kg of a 70 % w/w strength aqueous-alcoholic solution of tert-butyl hydroperoxide and 0.05 kg of emulsifier I in 0.35 kg of water followed by the addition of 0.17 kg of the Na salt of hydroxymethanesulfonic acid in 0.35 kg of water.

Feed 1: 55 kg of vinyl chloride
10 kg of vinyl propionate
35 kg of n-butyl acrylate
1.7 kg of emulsifier II
0.78 kg of emulsifier I and
41 kg of water

Feed 2: 0.003 kg of the Na salt of hydroxymethanesulfinic acid
0.125 kg of sodium acetate and
14 kg of water

Feed 3: 0.162 kg of sodium peroxydisulfate and
12 kg of water

Feed 4: 0.048 kg of sodium peroxydisulfate and
4 kg of water

Feed 5: 0.0018 kg of the Na salt of hydroxymethanesulfinic acid
0.0273 kg of sodium acetate and
4 kg of water

Emulsifier I: Na salt of the sulfated derivative of ethoxylated isooctyl phenol
(degree of ethoxylation: 25)

Emulsifier II: ethoxylated isooctyl phenol (degree of ethoxylation: 25)

D 2 to D 4: as D 1, except that the emulsion polymerization was carried out in the
sequence of operations stated above but at 60°, 70° and 80 °C
respectively, instead of 50 °C.

D 5 to D 8: as D 1 to D 4 in the sequence of operations stated above but with the
amount of sodium peroxydisulfate used increased by 50 % in each
case.

b) addition of basic agents as well as of active ingredients to the dispersions D 1
to D 8 and assessment of discoloration

The pH of the aqueous phase of the dispersions D 1 to D 8 was raised, in each
case, to a value of 8 by the addition of ammonia, KOH, NaOH and $\text{Ca}(\text{OH})_2$ after which

there were added in each case, based on the solids content of the aqueous dispersion, 0.1 % w/w of the following active substances, followed by visual assessment of the discoloration after a few days:

- 1 Benzaldehyde, camphor, benzyl alcohol, esters derived from formic acid and n-butanol, oleic acid, tetraethyl orthosilicate, bis(4-hydroxyphenyl)-sulfone, citric acid, salt of guanidine with hydrogen chloride (hydrochloric acid).

The use of ammonia gave distinct yellowing, whereas the use of KOH and NaOH
10 produced only a minimum yellow cast and the use of $\text{Ca}(\text{OH})_2$ gave no discoloration. The best degree of whiteness was exhibited by the dispersion which contained $\text{Ca}(\text{OH})_2$ and citric acid or $\text{Ca}(\text{OH})_2$ and the salt of guanidine with hydrogen chloride. The resulting fresh dispersions were subsequently processed to form film material,
15 stored in a desiccator cabinet at 50 °C for 14 days and again checked visually for discoloration. The results were the same as those obtained for the liquid condition. In all instances, the discolorations resulting from the use of the active ingredients of the invention were less pronounced than in the absence thereof, the action of citric acid and the salt of guanidine with hydrogen chloride being superior to that of sodium thiosulfate (comparative test), and the action of the other active substances was substantially equivalent to that of sodium thiosulfate.

We claim:

1. Aqueous polymer dispersion, obtainable by polymerizing, in aqueous medium by the free radical emulsion polymerization method, a mixture of monomers which contains from 10 to 100 % w/w of halogen-containing monomers, adjusting the pH of the aqueous phase of the resulting aqueous polymer dispersion to a value of from 5 to 10 by the addition of ammonia and primary and secondary amines of different basic agents and adding, based on the mixture of monomers, from 0.005 to 1 % w/w of at least one active ingredient selected from the group consisting of benzaldehyde, derivatives of benzaldehyde, having one or two C₁-C₄ alkyl radicals on the aromatic nucleus, benzyl alcohol, camphor, esters derived
10 from formic acid and C₃-C₆ alkanols, C₁₀-C₂₂-unsaturated fatty acids, tetraalkyl orthosilicates containing alkyl radicals of from 1 to 4 carbon atoms, bis(4-hydroxyphenyl)-sulfone, citric acid and the salts thereof as well as salts of guanidine with organic or inorganic acids, both the addition of the basic agents and that of at least one active ingredient being possible prior to, during, and/or
15 subsequently to the emulsion polymerization.

2. Aqueous polymer dispersion as claimed in claim 1, obtainable by using, as active ingredient, at least one selected from the group consisting of citric acid and salts thereof and salts of guanidine with organic or inorganic acids.

20 3. Aqueous polymer dispersion as claimed in claim 1, obtainable by using, as active ingredient, citric acid, the salt of guanidine with hydrogen chloride or a mixture of these active components.